



Heterogeneous catalytic wet peroxide oxidation of paraquat in the presence of modified activated carbon

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ABSTRACT

The catalytic wet peroxide oxidation (CWPO) method was applied to the degradation of paraquat, a widely used and highly toxic herbicide. The effect of ammonia pre-treatment and iron impregnation on Fenton-driven reaction efficiency was first investigated. Iron amendment and acidic oxygen-surface groups were found to promote the catalytic activity towards paraquat degradation. The effects of three significant operational parameters (hydrogen peroxide concentration, catalyst dosage and temperature) on catalytic performance of the most promising catalyst (AC-Fe) were then investigated. The best degradation yield (71.4% of COD abatement in a 20 mg L⁻¹ solution) was obtained with 12.5 mmol L⁻¹ H₂O₂, 1 g L⁻¹ catalyst dosage and *T* = 70 °C, although ambient temperature could be preferred for application convenience.

A nearly complete degradation of paraquat and its intermediates (~92% of COD removal) was achieved after 12 h treatment, when proceeding at ambient temperature via regular sequential additions of the spent amount of H₂O₂ in the presence of optimal catalyst dosage. A reasonably good stability of the catalyst was demonstrated during consecutive re-use of the same recovered sample, in long-term CWPO runs. Only a slight decrease of catalytic performance (from 92% to 85% of COD removal) was observed after five consecutive cycles, probably due to high stability of the supported iron species.

Time evolutions of aromatic intermediates and short-chain carboxylic acids were recorded using HPLC analysis, and clearly indicated that CWPO is capable of effectively degrading the paraquat herbicide.

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1. Introduction

The environmental impact of pesticides and herbicides has attracted much attention due to their increasing and widespread usage in agriculture to preserve crops from pests. In addition to direct spreading on cultures, important quantities of pesticides are discharged in the environment from applicator rinsates and industrial wastewaters generated from agricultural and veterinary factories. Generally due to their slow biodegradation and high mobility in the environment, these substances pass to surface and ground water, causing a potential danger for human and animal health. To reduce environmental and health impact of these pollutants, considerable human and economic resources were invested, over the past three decades, in the development of powerful and practical treatment processes for the degradation and/or removal of hazardous organic compounds from contaminated wastewaters.

Conventional wastewater treatment methods have limitations since most of pesticides are resistant to traditional chemical and biological treatments [1]. Among novel technologies developed during the past two decades, advanced oxidation processes (AOPs)

emerge as the most promising methods of depolluting contaminated water from applicator rinsates and industrial effluents, owing to their high potency to degrade and completely mineralize many refractory compounds including pesticides.

AOPs are those oxidation processes based on generation and use of powerful hydroxyl radicals ($\bullet\text{OH}$) by means of chemical, photochemical or photocatalytic methods. These radicals react unselectively and at a very high rate (*k* in the range of 10⁷ to 10¹⁰ M⁻¹ s⁻¹) with a wide range of organic compounds leading to their mineralization. Over the last three decades, several AOPs such as (conventional Fenton, photo-Fenton, electro-Fenton, O₃/UV, O₃/H₂O₂, H₂O₂/UV, UV/TiO₂ and plasma) have been conceptualized and successfully applied to the degradation of various organic compounds [2–10]. Nevertheless, Fenton reaction-based chemical oxidation still stands as the most studied degradation method in wastewater systems [11–15]. The conventional Fenton reagent is a well-known and very effective remediation system, based on the in situ generation of hydroxyl radicals via homogeneous reaction between hydrogen peroxide and ferrous ions or other low valence transition metal ions such as Cu(II), Co(II) and Mn(II). However, the necessary high dosage of iron and hydrogen peroxide, to achieve a high mineralization yield of the pollutant, as well as the continuous loss of catalyst and the important amount of generated iron hydroxide sludge, needing further separation

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step to comply with environmental regulations, constitutes the main evident drawbacks of the homogeneous Fenton system. One of the most practical and interesting ways proposed to circumvent these limitations is the use of Fenton-like heterogeneous catalysts involving iron minerals [16,17], crystalline $\text{Fe}_2\text{O}_3/\text{SBA-15}$ nano-composites [18] or transition metal ions immobilized on solid supports such as alumina [19], zeolites [20–22], pillared clays [23–25], ion exchange resin [26] and activated carbon [27]. This technology, known as catalytic wet peroxide oxidation (CWPO), represents a highly attractive alternative to classic Fenton method since it can promote the oxidation of different organic pollutants without sludge formation and with the possibility to recycle the iron catalyst. Since the early works of Fajferweg et al. [20] and Lücking et al. [28] reporting successful heterogeneous Fenton-like treatment of organic pollutants, numerous studies have aimed to develop and apply new solid catalysts to CWPO of model compounds and real industrial wastewaters [18,29]. Activated carbons offer most of desirable properties required for catalytic supports such as extended surface area, well-developed porosity and variable surface chemistry [30]. Therefore, they have attracted increasing interest over the last decade [27,28,31,32], which allowed a better understanding of the relation between the chemical and textural properties of the carbon and its catalytic efficiency. However, most of published studies were focused on the degradation of phenolic compounds and nothing had been reported concerning the application of CWPO method to the degradation of pesticide contaminants in the presence of active carbon supported catalyst.

Among numerous compounds, paraquat (PQ) (1,1'-dimethyl-4,4'-bipyridinium chloride) is one of the most widely used herbicides that is marketed as quick-acting, non-selective contact herbicide used at the weed emergence to protect a wide range of crops [33]. PQ is extremely toxic to mammalian and is considered as a potent human poison [34] that should be efficiently removed from contaminated wastewaters, in order to avoid its dangerous accumulation in the environment. Reviewing the literature revealed that there are only few reports investigating the degradation/mineralization of PQ by means of heterogeneous photocatalytic processes, in the presence of TiO_2 in slurry cell [35,36] or as immobilized films [37–39], or UV-ozonation method [40], and very recently, we reported the successful mineralization of PQ by electro-Fenton method [41].

The aim of this research was to study the catalytic wet hydrogen peroxide oxidation of paraquat in the presence of plain and modified activated carbons. The effects of various operational parameters including the AC surface chemistry, hydrogen peroxide concentration, catalyst dosage and working temperature on the kinetic of PQ degradation were carefully analyzed. The decay of paraquat and its degradation intermediates as well as the evolution of chemical oxygen demand (COD) were followed to verify the effectiveness of PQ degradation by CWPO method.

2. Experimental

2.1. Reagents

Unless otherwise stated, all chemicals and organic solvents used in this work were of analytical-reagent grade and used without further purification. Paraquat was an analytical standard purchased from Sigma (purity = 95–98%). Ammonia, sulfuric acid (98%), sodium chloride, ferrous sulfate, potassium iodide, ammonium heptamolybdate, o-phenanthroline, hydroxylamine and hydrogen peroxide (30%) were all purchased from Sigma–Aldrich (France). Methanol and acetonitrile (HPLC grade) were obtained from Pro-labo (France). Oxalic, Acetic, formic and succinic acids were

analytical grade products obtained from Fluka (France). Impurity-free nitrogen was used for solution de-oxygenation.

The activated carbon used in the present investigation was obtained from Panreac (France) with a particle size of 100–150 μm and a specific surface area, as measured by the BET method, of $986\text{ m}^2\text{ g}^{-1}$. Before usage, the original carbon was thoroughly washed in diluted hydrochloric acid (1 N) for 2 h in order to remove metal oxides components as well as residual physically adsorbed chemicals. Then the carbon was washed in boiling deionised water until circum-neutral pH of the supernatant, oven dried in thin layers at 105°C for 24 h and kept in desiccator until used. This sample is denoted as (AC).

2.2. Preparation and characterisation of activated carbon catalysts

The plain activated carbon was submitted to various treatments in order to produce catalysts with different surface chemistries. In the first step, plain carbon was treated with 2 M ammonia solution at 25°C for 2 h then thoroughly washed with deionised water until the pH of the supernatant was constant. Weighed portions of plain carbon (AC) and ammonia-treated carbon (AC_b) were subsequently impregnated with iron solution using a procedure adapted from Zazo et al. [27]. Calculated amount of ferrous nitrate to obtain 4% (w/w) of iron loading on the catalyst are dissolved in the minimum volume of deionised water sufficient to cover the activated carbon powder. After impregnation, all samples were left 2 h at room temperature, dried overnight at 60°C and finally calcinated at 200°C during 4 h. The resultant samples are labelled as (AC-Fe) and ($\text{AC}_\text{b-Fe}$).

Specific surface areas and pore volumes of the ACs were obtained from low temperature (77 K) nitrogen adsorption isotherms, using a computer controlled gas sorption analyser (ASAP 2000). Samples were outgassed overnight at 300 K prior to the adsorption analysis. The surface area, S_{N_2} , was calculated by applying the BET equation to the corresponding isotherms.

Surface functional groups were determined by standard neutralization-titration with HCl, NaOH, Na_2CO_3 , NaHCO_3 (0.05 N in water) according to the Boehm procedure [42].

The point of zero charge (pH_{PZC}), was determined by the so-called pH drift method according to the procedure described in the literature [43,44].

2.3. Adsorption and CWPO degradation procedure

All degradation assays were carried out in magnetically stirred 250 mL stoppered conical flasks wrapped in aluminum foil and filled with 200 mL of 20 mg L^{-1} paraquat solution. The solution pH was adjusted to 3.0, using sulphuric acid and a Mettler-Toledo 340 pH-meter, to favor an optimum generation of hydroxyl radicals [4]. Treatment was initiated by simultaneous addition of 50 mg powdered catalyst and the required amount of hydrogen peroxide (30%, v/v). The effect of hydrogen peroxide dosage was investigated by amending various initial concentrations corresponding to 1, 2, 5, 10 and 20 times the theoretical stoichiometric amount of H_2O_2 needed for complete mineralization of paraquat (2.41 mmol L^{-1}). To assess the role of temperature, this parameter was controlled within $\pm 1^\circ\text{C}$ at the desired value (30, 40, 50, 60 and 70°C) by immersing the reaction flask in a constant temperature water bath.

At regular time intervals, small volume samples (1 mL) were withdrawn from reaction flask and immediately filtered through $0.2\text{ }\mu\text{m}$ PTFE syringe top filters to remove carbon particles. The sample was then analyzed to follow the degradation of paraquat and its intermediates. To obtain quantitative mineralization of PQ, long-term assays were carried out in the presence of 1 g L^{-1} of the

Table 1

Selected textural properties and surface functional groups of plain and modified activated carbon catalysts.

Activated carbon	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{micro} ($\text{m}^2 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	Mean pore diameter (nm)	pH_{pzc}	Surface functional groups (mmol g^{-1})			
						Carboxylic	Lactone	Phenolic	Basic
AC	986	570	0.326	1.93	5.4	0.15	0.25	0.05	0.25
ACb	1004	594	0.338	1.91	6.5	0.05	0.25	0.05	0.50
AC-Fe	822	476	0.264	1.82	3.5	0.25	0.80	0.15	0.02
ACb-Fe	834	490	0.280	1.79	4.1	0.15	0.75	0.20	0.05

most promising catalyst. In these trials, the spent amount of H_2O_2 was supplemented to the reaction flask in three regular sequential applications over 12 h of treatment time, in order to maintain optimum oxidation conditions.

Paraquat adsorption assays were carried out in the same conditions, in the presence of 25 mg L^{-1} of paraquat without hydrogen peroxide addition. Upon completion of adsorption equilibrium, the activated carbon powder was separated from the water phase by centrifugation for 10 min, then desorption was started by adding 100 mL of deionised water of pH 3.0. The freely dissolved paraquat was determined at various time points by HPLC analysis. In the same way, hydrogen peroxide decomposition runs were performed in pure aqueous solutions in the absence of paraquat herbicide.

2.4. Analytical methods

The decay of paraquat concentration and the evolution of its aromatic degradation products in treated samples were measured with a Beckman HPLC consisting of an isocratic LC pump, a Rheodyne injection valve ($20 \mu\text{L}$) and a diode array detector (DAD). The separation was achieved on an ODS-18 ($5 \mu\text{m}$, $25 \text{ cm} \times 4.6 \text{ mm}$ (i.d.)) reversed phase supplied by Supelco (Supelco, Inc., Bellefonte, PA) and the mobile phase consisted of 100 mM sodium chloride and 0.1% decanesulfonic acid dissolved in acetonitrile/water (25/75, v/v) delivered at a flow rate of 1 mL min^{-1} . The pH was adjusted to 2.5 with phosphoric acid. The detector wavelength was set at 220–280 nm for paraquat and its main degradation products. Under the described analytical conditions, the paraquat retention time was approximately 7.6 min, while its degradation products were eluted between 4 and 5.5 min.

Generated carboxylic acids were monitored by ion-exclusion chromatography using the same above-described chromatograph fitted with a Supelcogel H column ($9 \mu\text{m}$, $25 \text{ cm} \times 4.6 \text{ mm}$ (i.d.)) at 40°C and setting the (DAD) wavelength at 210 nm. The mobile phase was 4 mM H_2SO_4 pumped at 0.2 mL min^{-1} .

To assess the progress of paraquat and its intermediates degradation, the COD removal was monitored using the procedure described in the standard method [45]. The obtained values were corrected from hydrogen peroxide interference using the equation proposed by Kang et al. [46]:

$$\text{COD} = \text{COD}_{\text{exp}} - 0.4706[\text{H}_2\text{O}_2] \quad (1)$$

where COD_{exp} is the experimentally measured COD value (in mg L^{-1}) and $[\text{H}_2\text{O}_2]$ is the hydrogen peroxide concentration detected in the measured sample by iodometric method (in mg L^{-1}). Nitrate ions were measured following the salicylate spectrophotometric method [47], while ammonium was analyzed by potentiometric flow-injection method using a gas-diffusion cell [48].

Hydrogen peroxide and leached iron concentrations were determined spectrophotometrically using a Beckman spectrophotometer (DU 640B) according to the iodometric and o-phenanthroline method, respectively.

3. Results and discussion

3.1. Textural and surface chemistry characterization of the catalysts

The results of textural analysis, PZC measurements and Boehm's titrations following surface modifications are quoted in Table 1. It is clear from these results that ammonia treatment enhances the basic properties of the carbon at the expense of their surface acidic oxygenated groups, without any significant change of surface area or porous structure. The PZC measurements corroborate this conclusion since AC_b sample presents a higher PZC value than virgin carbon. Taking into account the mild conditions used during ammonia treatment, the obtained results can be, at least, partially attributed to neutralization of acidic surface groups (mainly carboxylic groups). On the other hand, iron amendment was found to produce measurable reduction in BET specific surface area with a concomitant decrease in pore volume, attributed to blockage of the narrow pores entries by Fe_2O_3 aggregates formed during iron impregnation and calcinations, as proved by Zazo et al. [27] based on XPS measurements. In addition, the presence of iron led to lower pH_{PZC} values and substantially increased the total concentration of surface oxygen groups which is a factor of 2 to 3 times higher than in Fe-unamended carbon. Similar tendency was reported in the literature [49] and was ascribed to oxidizing character of ferric species which promote the generation of new surface oxygen groups during the impregnation and calcination steps. It is interesting to note here that undesirable reduction of catalyst activity related to surface area loss following iron amendment should be largely balanced by the positive effect of iron loading.

3.2. Adsorption and desorption kinetics of paraquat

In order to discriminate between the contributions of simple adsorption and catalytic oxidation processes to the removal of paraquat, kinetics of adsorptive removal of the herbicide by the virgin and modified activated carbon supports were investigated without H_2O_2 addition (Fig. 1). A relatively rapid initial adsorption was observed with all supports, since more than 75% of the equilibrium levels were achieved after 90 min of contact time. The recorded abatements of paraquat clearly show that all carbon supports have high adsorption capacities reaching 78.4, 94.8, 62.5 and 86.1 mg g^{-1} for AC, AC_b, AC-Fe and AC_b-Fe, respectively. Ammonia treatment enhanced paraquat uptake probably due to the observed decrease of acidic surface oxygen-containing groups, leading to significant increase of π electron density of the graphene layers and stronger dispersive interaction between free electrons in paraquat molecules and AC surface. On the opposite, it is observed that iron amendment clearly decreases the paraquat uptake of carbon supports. This could be ascribed to the observed surface area and pore volume loss following iron amendment, as well as to enhancement of surface acidity.

On the other side, a rapid re-equilibration was achieved during the desorption step, performed by contacting the saturated carbon supports with fresh deionised water of pH 3.0. Indeed, only 45 min

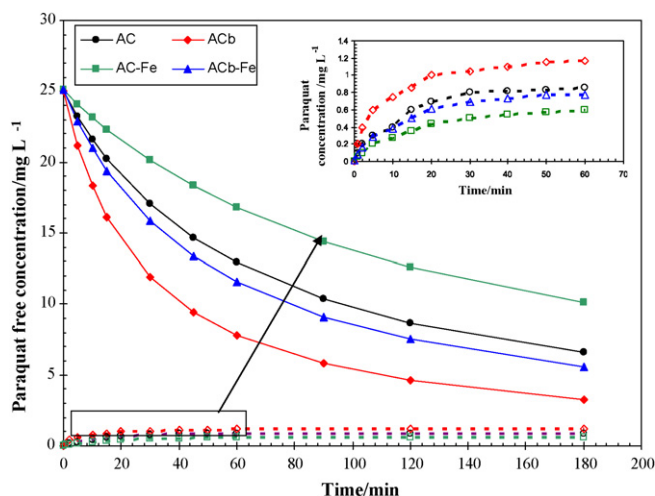


Fig. 1. Sorption and desorption kinetics of paraquat onto plain and modified activated carbons (AC, ACb, AC-Fe and ACb-Fe). Experimental conditions: $T = 25^\circ\text{C}$, $\text{pH} = 3.0$, mass of activated carbon = 50 mg, $[\text{Paraquat}]_0 = 25 \text{ mg L}^{-1}$.

were sufficient to reach the equilibrium concentrations, which are found to be lower than 1 mg L^{-1} . These findings proved the negligible leaching and the tight attachment of adsorbed paraquat to the catalyst surface and clearly showed the fast character of paraquat adsorption–desorption process, pointing out the relatively high performance of all investigated carbon supports for adsorption removal of this herbicide. To study the individual contribution of catalytic oxidation process, carbon catalysts will be pre-saturated with paraquat for all further investigations.

3.3. Catalytic activity

3.3.1. Hydrogen peroxide decomposition

The catalytic decomposition of hydrogen peroxide was studied in the presence of the as-prepared and paraquat pre-saturated catalysts. The measured kinetics of H_2O_2 decay followed a pseudo-first order model as illustrated in Fig. 2. The H_2O_2 reaction rate constants calculated as the slopes of semilog plots of H_2O_2 concentration versus time are also provided in Fig. 2. It can be observed that both ammonia treatment and iron amendment enhanced effectively the H_2O_2 decomposition rate. These findings are in agreement with other published studies [49–51], reporting that acidic oxygen-surface groups decrease the H_2O_2 decomposition rate considerably. Such behaviour is consistent with the mechanism considered by Bansal et al. [52] assuming that H_2O_2 decomposition could be initiated by the exchange of a surface hydroxyl group with a hydrogen peroxide anion. According to this mechanism, the decomposition rate of H_2O_2 , acting as a weak acid ($\text{p}K_a = 11.6$) should be enhanced by a more basic character of the catalyst surface. On the other hand, it is well established that carbon-bound Fe promotes hydrogen peroxide decomposition towards the generation of hydroxyl radicals, according to a Fenton-like reaction, leading to a faster H_2O_2 decay.

Furthermore, the H_2O_2 decomposition rates in the presence of pre-adsorbed paraquat exhibit the same trend found with as-prepared catalysts. Nevertheless, significant decreases of reaction rates are observed in the presence of pre-adsorbed paraquat. This could be attributed to reduction of surface active sites which are hindered by adsorbed paraquat and no longer available to react with H_2O_2 .

The observed differences between activities of tested catalysts towards the hydrogen peroxide decomposition should greatly affect their performances during CWPO treatment of paraquat.

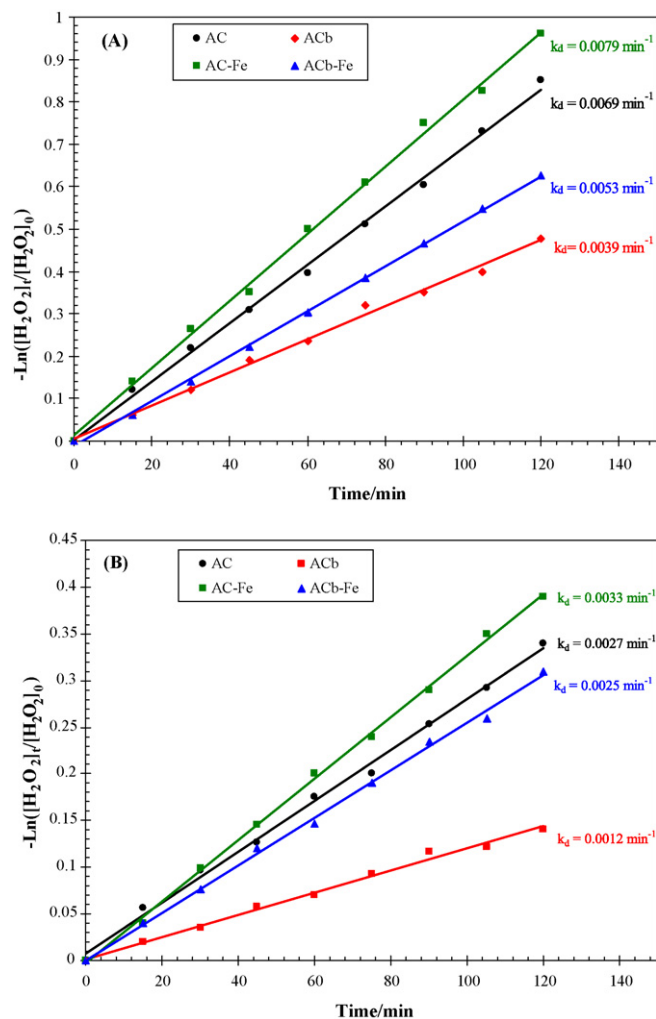


Fig. 2. Catalytic hydrogen peroxide decomposition in the presence of the as-prepared (A) and paraquat pre-saturated (B) carbon catalysts. Experimental conditions: $T = 25^\circ\text{C}$, $\text{pH} = 3.0$, $V_0 = 200 \text{ mL}$, $[\text{H}_2\text{O}_2]_0 = 25 \text{ mmol L}^{-1}$, catalyst dosage = 0.25 g L^{-1} .

3.3.2. Heterogeneous catalytic wet peroxide oxidation of paraquat

Catalytic oxidation assays of paraquat by H_2O_2 were carried out in the presence of 0.25 g L^{-1} of pre-saturated catalysts. The obtained degradation results are presented in Fig. 3 in terms of paraquat concentration and COD decays upon time. Results of paraquat degradation by the sole action of H_2O_2 without any catalyst addition are also included to assess its relative contribution to the removal process. In the absence of catalyst, hydrogen peroxide produced only very low oxidation of paraquat (less than 5% after 3 h), indicating its negligible contribution to observed paraquat decays. In contrast, highly significant removal yields (between 60 and 84% after 3 h) were observed in the presence of all investigated catalysts. The measured removal yields increased in the following order $\text{ACb} < \text{AC} < \text{ACb-Fe} < \text{AC-Fe}$. It appears that oxidation efficiency is reduced in the presence of ammonia-treated catalysts in spite of higher H_2O_2 decomposition rates as compared to untreated ones. Presumably, this could be ascribed to a faster decomposition of H_2O_2 into non-reactive O_2 and H_2O species. Another possible explanation could be related to a possible competition between paraquat and H_2O_2 for the same sites, as suggested by Santos et al. [53] when studying the decolourisation of dye solutions by oxidation with H_2O_2 in the presence of activated carbon as catalyst. Such argument is in perfect agreement with the observed lower catalytic activity of

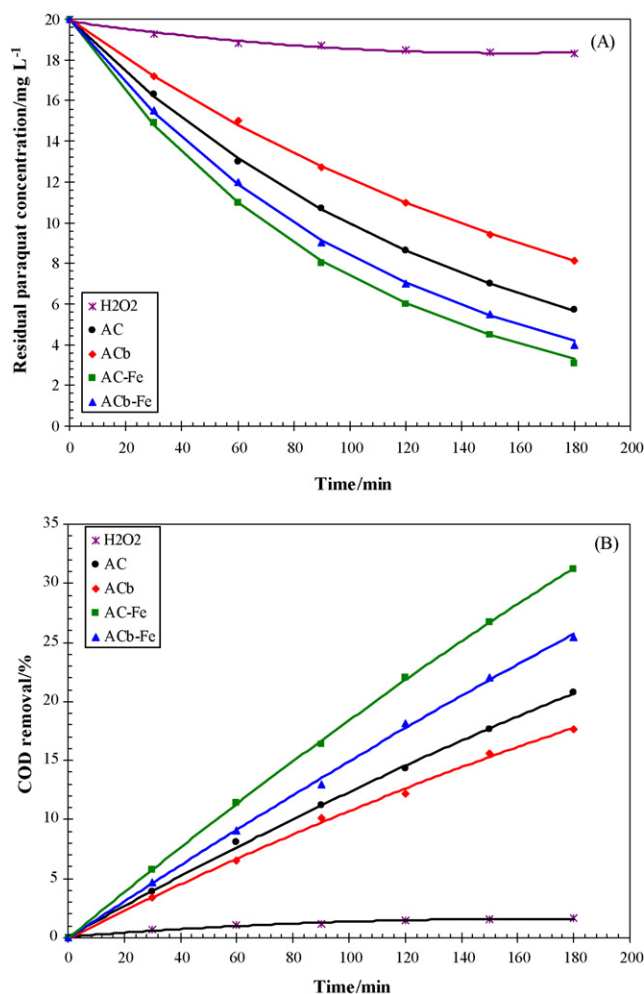


Fig. 3. Paraquat (A) and COD (B) removals upon treatment with H₂O₂ in the absence and presence of ammonia-treated and untreated Fe-amended (AC_b-Fe, AC-Fe), and Fe-unamended carbons (AC, AC_b). Experimental conditions: $T = 25^\circ\text{C}$, $\text{pH} = 3.0$, $V_0 = 200\text{ mL}$, $[\text{H}_2\text{O}_2]_0 = 12.05\text{ mmol L}^{-1}$, $[\text{Paraquat}]_0 = 20\text{ mg L}^{-1}$ ($\text{COD}_0 \approx 38.6\text{ mg L}^{-1}$), catalyst dosage = 0.25 g L^{-1} .

AC_b and AC samples which have higher adsorption affinity towards paraquat, leading to the filling of a higher fraction of active sites which are no longer available to react with hydrogen peroxide.

On the other hand, iron amendment was found to markedly enhance paraquat oxidation as evidenced from the high removals of COD (31% and 23.7% in the presence of AC-Fe and AC_b-Fe, respectively) as compared to Fe-unamended samples (20.7% and 17.5% in the presence of AC and AC_b, respectively). Such behaviour is in agreement with the well-known fact that carbon-bound Fe promotes H₂O₂ decomposition into highly reactive $\bullet\text{OH}$ radicals. It is interesting to note that the observed increase of acidic oxygen-surface groups associated to iron loading, could participate in retarding H₂O₂ decomposition into O₂ and H₂O, increasing by the way the amount of hydrogen peroxide available for reacting with bound-iron to produce $\bullet\text{OH}$ radicals [27,51].

To investigate the possibility of homogeneous contribution to the herbicide oxidation, concentrations of freely dissolved iron were analyzed at the end of the treatments and found to be lower than 0.2 mg L^{-1} , attesting a very low leaching of carbon-bound Fe on all investigated catalysts. Based on this finding, oxidative degradation of paraquat was investigated in the presence of 0.2 and 1 mg L^{-1} of dissolved iron. The recorded COD removal after 3 h was found to be 2 and 4%, respectively, indicating a relatively low contribution of homogeneous phase reaction. Thus it was concluded that

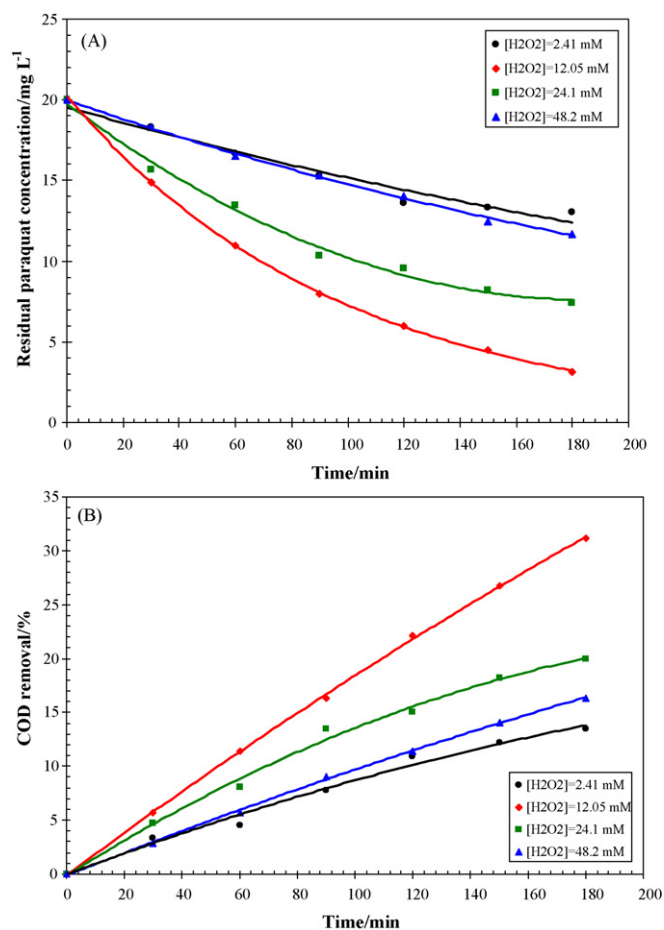


Fig. 4. Effect of hydrogen peroxide concentration on paraquat (A) and COD (B) decays with electrolysis time during CWPO in the presence of AC-Fe catalyst. Experimental conditions: $T = 25^\circ\text{C}$, $\text{pH} = 3.0$, $V_0 = 200\text{ mL}$, $[\text{Paraquat}]_0 = 20\text{ mg L}^{-1}$ ($\text{COD}_0 \approx 38.6\text{ mg L}^{-1}$), catalyst dosage = 0.25 g L^{-1} .

the observed catalytic removal of paraquat was dominated by the heterogeneous reaction with bound iron at the catalyst surface. All these findings provide supporting evidences on the high potency of CWPO method to achieve efficient degradation of paraquat, in the presence of iron-loaded activated carbon catalyst.

To get deeper insight into the oxidation process and optimize the degradation efficiency, a methodical study of the effects three significant operational parameters (H₂O₂ dosage, catalyst concentration and temperature) was carried out in the presence of the most promising catalyst (AC-Fe).

The time-course evolutions of paraquat and COD abatements in the presence of variable initial concentrations of H₂O₂ (in the range 2.41–48.2 mM corresponding to 1–20 times the theoretical stoichiometric amount of H₂O₂ needed for complete mineralization of paraquat) are depicted in Fig. 4. As can be seen, paraquat removal rate and efficiency increased upon increasing H₂O₂ concentration from 2.41 to 12.05 mM, likely due to a significant acceleration of $\bullet\text{OH}$ production as well as propagation reactions that form transient oxygen reactive species that aid in the destruction of organic pollutant [54]. A maximum COD abatement of 31.2% was obtained at H₂O₂ concentration of 12.05 mM after 3 h of treatment. No further improvements were observed with higher H₂O₂ concentrations. In contrary, relatively important drops in oxidation performances were recorded at high H₂O₂ dosages, likely due to its well-known scavenging effect towards hydroxyl radicals according to the fol-

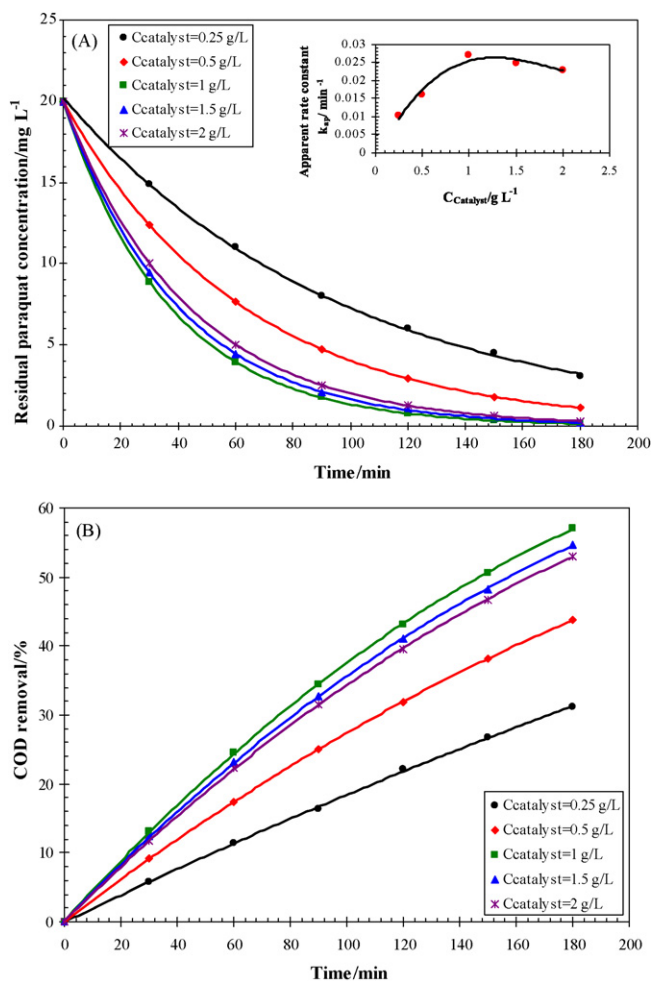


Fig. 5. Effect of catalyst dosage on paraquat decay (A) and COD removal (B) during CWPO treatment in the presence of AC-Fe catalyst. The inset shows pseudo-first order rate constant evolution with catalyst concentration. Experimental conditions: $T = 25^\circ\text{C}$, $\text{pH} = 3.0$, $V_0 = 200\text{ mL}$, $[\text{H}_2\text{O}_2]_0 = 12.05\text{ mmol L}^{-1}$, $[\text{Paraquat}]_0 = 20\text{ mg L}^{-1}$ ($\text{COD}_0 \approx 38.6\text{ mg L}^{-1}$).

lowing reactions [55]:



This parasitic phenomenon produced a dramatic loss of hydrogen peroxide leading to oxidation inefficiency and significant undesirable increase of operational cost. Therefore, a 12.05 mM concentration of H_2O_2 will be used for subsequent studies.

The influence of catalyst dosage, varying between 0.25 and 2 g L⁻¹, on PQ and COD abatements was also evaluated and is presented in Fig. 5. As expected, removal efficiency increased in the presence of higher catalyst concentration, due to the increasing number of active catalytic sites available for H_2O_2 decomposition. It is interesting to remember that adsorption do not play any significant role in the observed improvement, since the used catalysts were pre-saturated with PQ. The oxidation kinetic followed a pseudo-first-order model as widely accepted and experimentally confirmed for Fenton-like oxidation of several organic compounds [9,56]. The apparent pseudo-first order rate constant was found to increase linearly with catalyst concentration in the range (0.25–1 g L⁻¹), but slowed down beyond these values, probably due to significant increase of bound-iron scavenging effect towards hydroxyl radicals [57–59]. Relatively fast degradation of paraquat

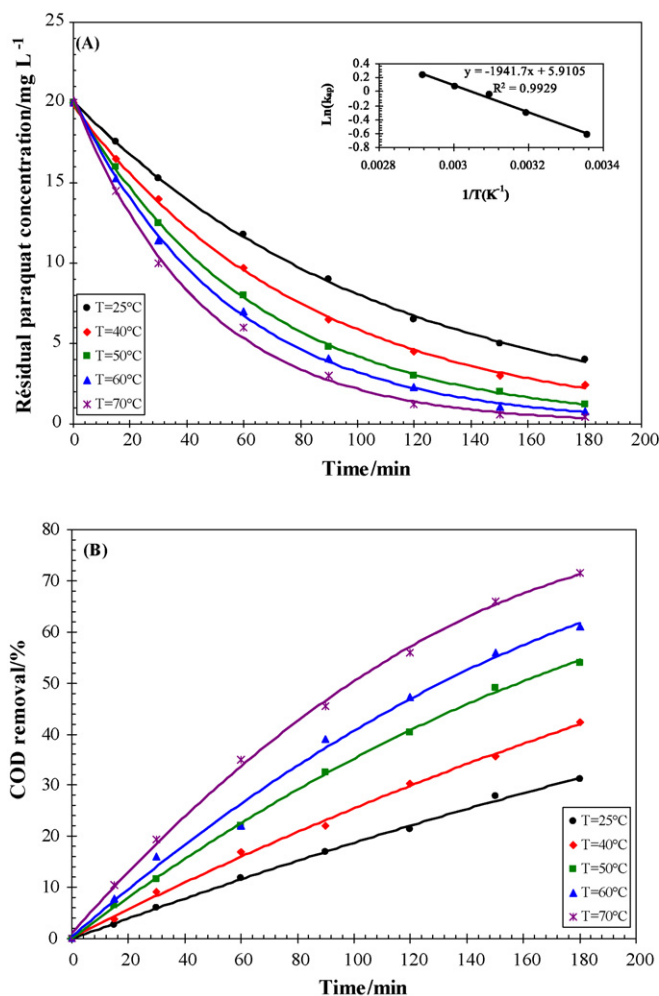


Fig. 6. Effect of temperature on paraquat (A) and COD (B) removals during CWPO treatment in the presence of AC-Fe catalyst. The inset shows Arrhenius model analysis. Experimental conditions: $\text{pH} = 3.0$, $V_0 = 200\text{ mL}$, $[\text{H}_2\text{O}_2]_0 = 12.05\text{ mmol L}^{-1}$, $[\text{Paraquat}]_0 = 20\text{ mg L}^{-1}$ ($\text{COD}_0 \approx 38.6\text{ mg L}^{-1}$), catalyst dosage = 0.25 g L⁻¹.

and its intermediates (~60% of COD removal after 3 h of treatment time) was achieved using 1 g L⁻¹ of AC-Fe catalyst.

The comparative results of PQ oxidation and COD abatements obtained at five different temperatures ranging from 25 to 70 °C (Fig. 6), in the presence of 12.05 mM H_2O_2 and 0.25 g L⁻¹ of CA-Fe catalyst, showed significant improvement of removal efficiency upon increasing temperature. Nearly complete (98%) removal of PQ and 71% abatement of COD were obtained at 70 °C after 3 h of treatment, while only 80% and 31% of paraquat and COD removals were achieved at 25 °C. The pseudo-first-order rate constant evolution with temperature was in accordance with the Arrhenius equation and the corresponding activation energy was determined as 16.1 kJ mol⁻¹. Enhanced paraquat degradation measured at higher solution temperature could be reasonably attributed to an increase in paraquat and H_2O_2 diffusion as evidenced by Kan and Huling [60]. Nevertheless, taking into account application convenience and operational cost, ambient temperature may be preferred although higher temperatures could be employed when faster degradation rate is required.

3.4. Paraquat mineralization and evolution of degradation intermediates

To achieve quantitative removal of PQ herbicide and its intermediates and further understand its degradation pathway, long-term

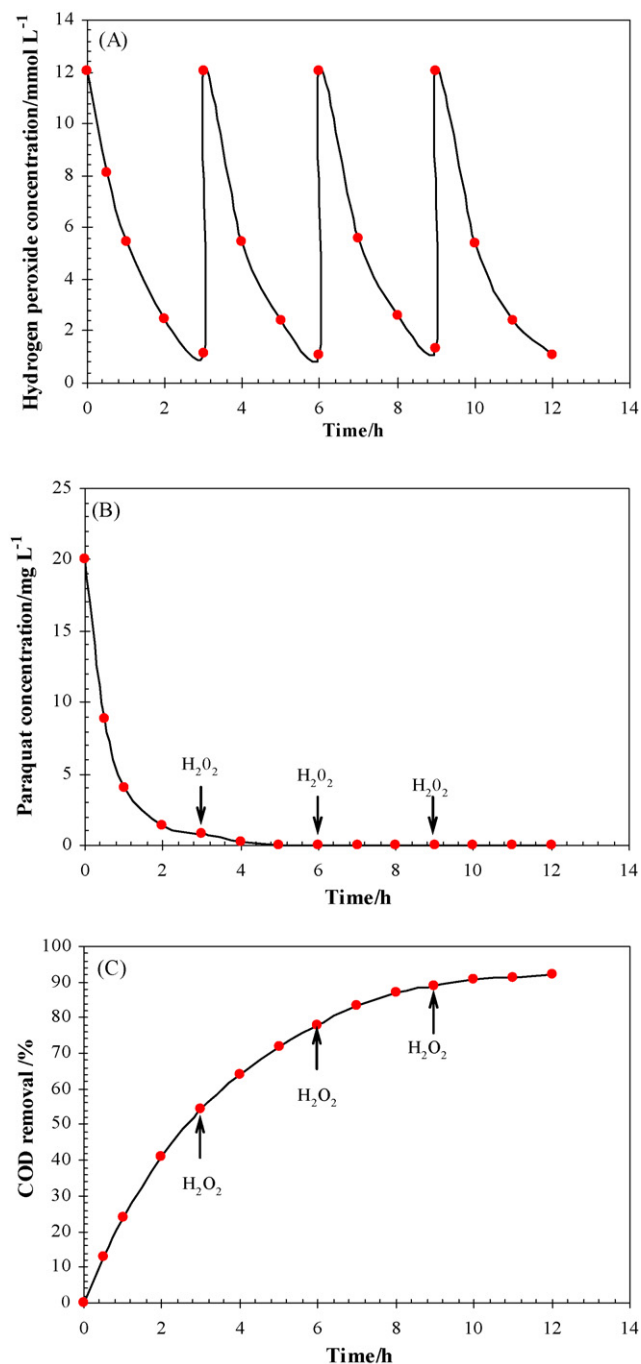


Fig. 7. Hydrogen peroxide decomposition (A), paraquat concentration decay (B) and COD removal (C) during long-term CWPO assay in the presence AC-Fe catalyst. Experimental conditions: $T=25^{\circ}\text{C}$, $\text{pH}=3.0$, $V_0=200\text{ mL}$, $[\text{H}_2\text{O}_2]_0=12.05\text{ mmol L}^{-1}$ (with three additional applications over 12 h of treatment), $[\text{Paraquat}]_0=20\text{ mg L}^{-1}$ ($\text{COD}_0\approx 38.6\text{ mg L}^{-1}$), catalyst dosage = 1 g L^{-1} .

assay was performed over 12 h by supplementing the lost amount of H_2O_2 in regular sequential applications in order to reduce spikes in H_2O_2 concentration and $\bullet\text{OH}$ scavenging. The time evolutions of COD abatement as well as paraquat concentration and its stable degradation intermediates, generated during mineralization, were recorded. Data shown in Fig. 7 indicate a total removal of paraquat in less than 4 h with a nearly complete degradation of its intermediates, as evidenced from the high abatement of COD (more than 92% at the end of the treatment). The HPLC profiles of samples collected at various time points throughout CWPO treatment, showed a relatively rapid disappearance of the peak cor-

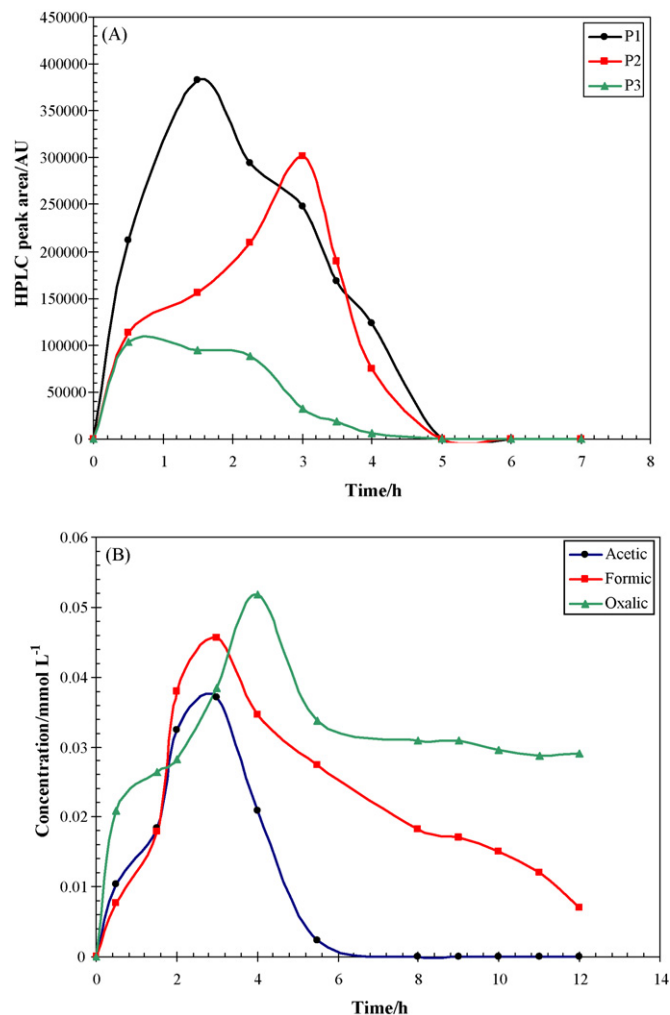


Fig. 8. Time evolution of aromatic intermediates (A) and aliphatic carboxylic acids (B) generated during long-term CWPO assay. Experimental conditions: $T=25^{\circ}\text{C}$, $\text{pH}=3.0$, $V_0=200\text{ mL}$, $[\text{H}_2\text{O}_2]_0=12.05\text{ mmol L}^{-1}$ (with three additional applications over 12 h of treatment), $[\text{Paraquat}]_0=20\text{ mg L}^{-1}$ ($\text{COD}_0\approx 38.6\text{ mg L}^{-1}$), catalyst dosage = 1 g L^{-1} .

responding to PQ ($t_R=7.6\text{ min}$), accompanied by the appearance of three new peaks (P1–P3), which elute before the parent compound ($t_{R1}=4.4\text{ min}$, $t_{R2}=4.9\text{ min}$ and $t_{R3}=5.2\text{ min}$) and attributed to aromatic oxidation intermediates. Although these intermediates were not conclusively identified, since it was not the aim of this study, it is interesting to note that they were identical to those detected during the electro-Fenton oxidation of PQ [41] and may presumably correspond to demethylation products (such as 4,4'-bipyridine and monopyridone) and hydroxylation or oxidative ring cleavage products (such as 4-carboxy-1-methyl-pyridinium ion, 4-picolinic acid and hydroxyl-4-picolinic acid), as suggested by Kearney et al. [40] when studying PQ degradation by UV-ozonation. The aromatic oxidation intermediates are rapidly degraded as inferred from their quick disappearance (in almost 5 h) after reaching their peak concentration (Fig. 8A). This behaviour is consistent with the effective measured paraquat and COD removals and evidenced that the generated aromatic intermediates can further react with $\bullet\text{OH}$ leading to relatively rapid sequential formation of aliphatic carboxylic acids as illustrated in Fig. 8B. Three aliphatic carboxylic acids: oxalic, acetic and formic were identified and their evolutions during treatment were followed by ion-exclusion chromatography. The absence of succinic acid is in apparent contrast with our findings in previous work on the electro-Fenton degradation of PQ

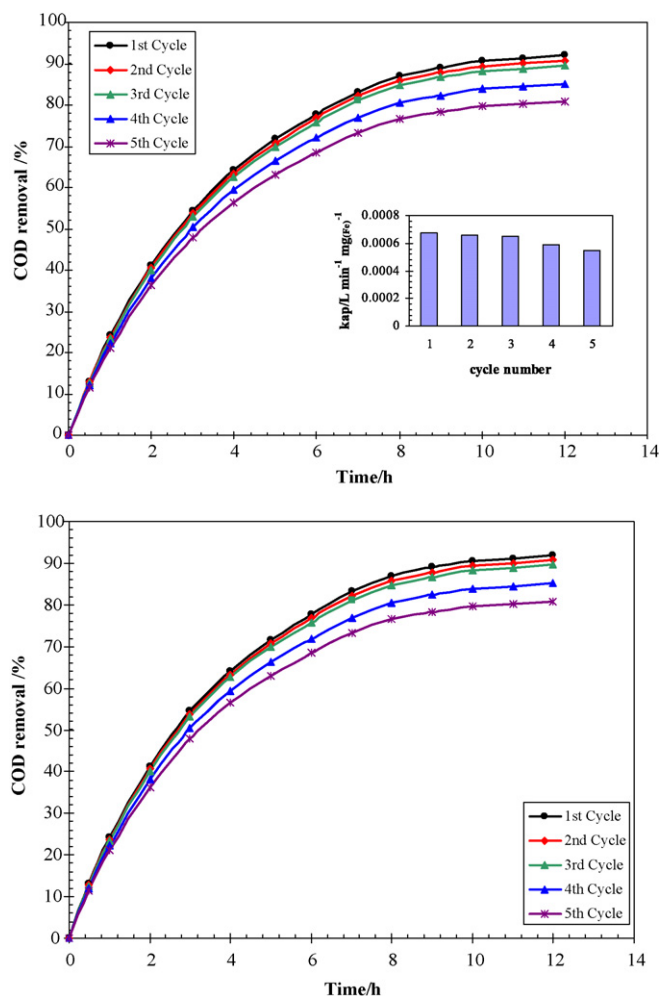


Fig. 9. Comparison of catalytic performances obtained during five consecutive re-uses of AC-Fe catalyst in long-term CWPO experiments. The inset shows changes of the apparent rate constants normalized by the mass of iron present on the catalyst support at the beginning of each cycle. Experimental conditions: $T=25^{\circ}\text{C}$, $\text{pH}=3.0$, $V_0=200\text{ mL}$, $[\text{H}_2\text{O}_2]_0=12.05\text{ mmol L}^{-1}$ (with three additional applications over 12 h of treatment), $[\text{Paraquat}]_0=20\text{ mg L}^{-1}$ ($\text{COD}_0\approx 38.6\text{ mg L}^{-1}$), catalyst dosage = 1 g L^{-1} .

[41], pointing out an outstanding difference in the reaction pathway of CWPO. As can be seen from Fig. 8B, short-chain carboxylic acids are generated as soon as the electrolysis is started, reaching their maximum concentrations after approximately 3 h of treatment, and tapered off slowly thereafter. At the end of the treatment, formic and oxalic acids were not completely removed since significant residual concentrations were recorded. In contrast, acetic acid was totally reduced after approximately 6 h of reaction time. Simultaneous gradual accumulations of nitrate and ammonium ions were recorded, reaching 65% and 26% of initial nitrogen content in paraquat, respectively, at the end of treatment. Under studied experimental conditions, a very low iron leaching was measured during the first 6 h of treatment (only 0.28 mg L^{-1} , corresponding to 0.7% of loaded iron), whereas a significantly higher leaching was observed at the end of the treatment (almost 1.3 mg L^{-1} , corresponding to 3.2% of loaded iron). This could be ascribed to the observed increase of oxalic acid concentration leading to formation of stable ferric-oxalato complexes. All these findings provide clear evidences that CWPO in the presence of iron-impregnated activated carbon catalyst could be considered as an attractive, cost-effective and user friendly treatment method for the remediation of paraquat contaminated wastewaters.

3.5. Catalyst re-use and stability

Investigation of catalyst stability in long-term reactions is of crucial importance for evaluating its applicability for industrial and real wastewaters treatment. Fig. 9 shows the PQ removal by five consecutive CWPO runs performed with the same catalyst sample, recovered by filtration and thoroughly washed with water, after each cycle. As can be seen, COD abatement was slightly dropped from 92% to 84% in the fifth consecutive cycle, indicating that the recycled catalyst could be used more than five times with no dramatic deactivation. The measured loss of activity could be, at least partially, attributed to cumulative leaching of iron species from catalyst support. Nevertheless, the apparent pseudo-first-order rate constants normalized by the effective amount of iron present on the catalyst support at the beginning of each cycle showed a slight decrease with increasing cycle number (inset of Fig. 9). This behaviour shows that iron leaching is not the only reason for the observed loss of activity and point out the possible occurrence of iron deactivation as observed by Ramirez et al. [61].

These results evidenced the reasonably good stability of AC-Fe catalyst and confirmed the high potency of the investigated method for real wastewater remediation.

4. Conclusion

The heterogeneous catalytic removal of paraquat with hydrogen peroxide in the presence of four different activated carbon catalysts was studied. The catalytic activity towards paraquat degradation was found to be enhanced by both acidic oxygen-surface groups and bound-iron species. The effects of several operational parameters (H_2O_2 concentration, catalyst dosage and temperature) were investigated in the presence of the most promising catalyst. Complete degradation of paraquat and high COD abatement (almost 92%) were achieved with 4 sequential additions of hydrogen peroxide (12.05 mmol L^{-1} per application), in the presence of 1 g L^{-1} of AC-Fe catalyst. Paraquat degradation generated three aromatic intermediates which underwent subsequent oxidative ring opening reactions leading to three short-chain aliphatic acids (acetic, formic and oxalic), as identified by ion-exclusion chromatography. Consecutive re-use of AC-Fe sample in long-term trials, proved the relatively good stability of the catalyst since only a slight decrease of catalytic performance was observed. Thus, CWPO seems to be a reliable option for treatment, on small scale, of industrial or agricultural wastewaters contaminated with paraquat.

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